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Archives of Applied Science Research, 2013, 5 (4):36-45
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

A study on liquid waste control measures practiced in Khartoum refinery

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ABSTRACT

This study has been conducted to assess the liquid waste control measures practiced in the Khartoum refinery to investigate the control measures which are applied to minimize the quantity of the liquid waste produced, or to treat them in a way that they could not cause any harmful effects to the receiving environment. A survey was carried on the liquid wastes, solid wastes and gaseous emissions to identify their source, treatment, disposal methods and characteristics. Laboratory analysis were carried out for liquid waste from four locations, starting from grid pond before treatment, physical treatment unit, Biological Oxygen Demand and chemical treatment and oxidation ponds. The laboratory analysis covered the following parameter: oil content, chemical oxygen demand (COD), total dissolved solids (TSS), sulphides, nitrogen ammonia (NH_3-N), biochemical oxygen demand (BOD) and pH. The result obtained showed that the oil content is exceed the limits, also chemical oxygen demand (COD) and total suspended solids (TSS) exceed the limits set out by Sudanese Petroleum Corporation (Regulation for Protection of the environment in the petroleum industry 2001). Also trace elements, cadmium, iron and lead exceed the limits as estimated in appendix (1) and appendix (2). After a time it will accumulates and pollute water and soil, therefore it should be control during the process by minimizing the quantity or to be recycling after treatment.

INTRODUCTION

Environment generally means all physical, chemical and biological agents together with the social factors capable of having direct or indirect effect, immediately or in the long run, on living organisms and human activities considered in a given time frame. Environment protection means maintaining or re-establishing natural state of the environment of mankind, animals, plants and landscape. Environmental compatibility is an Indication for degree of impact on the environment of a measure that has been programmed or already implemented. Compatibility with the environment is an important objective in the field of environment protection. The early assessment of this compatibility makes it possible in the planning phase of a project to prevent repercussions that are harmful to the environment by minimizing or to limit them within acceptable properties. Pollution is defined as an undesirable change in the physical, chemical, or biological characteristics of the air, water, or land that can harmfully affect health survival or activities of humans or other living organisms (National Academy of Science 1969 b).Pollution arises from the presence of materials that are foreign to the body of air, water and land. On an international scale, air pollution is caused by burning fossil fuels, such as oil, natural gas and coal etc. Today, countless air pollutants are emitted everyday by cars and other motor vehicles. Some of these pollutants include carbon monoxide, oxides of nitrogen and hydrocarbons such as butane and methane. Some of these air pollutants can be very poisonous even in low concentrations .Water pollution occurs when a body of water is adversely affected due to the addition of large amounts of materials to the water. When it is unfit for its intended use, water is considered polluted. Comprising over 70% of the Earth's surface, water is undoubtedly the most precious natural resource that exists on our

planet. Two types of water pollutants exist; point source and nonpoint source. Point sources of pollution occur when harmful substances are emitted directly into a body of water. Oil spill best illustrates point source water pollution; a nonpoint source delivers pollutants indirectly through environmental changes. An example of this type of water pollution is when fertilizer from a field is carried into a stream by rain, in the form of run-off which in turn affects aquatic life.

The petroleum industry has made remarkable contribution to modern civilization. It has made possible services of modern transport systems on land, at sea and in the air, the petrochemical industry, has made possible the production of countless chemicals that touch every aspects of our daily living .The major aim of treating hazardous wastes is to modify the physical and chemical properties of the wastes so that they will have less or no impacts on health and environment or to render it more amenable for final disposal. The treatment techniques can be physical, chemical or biological [20]. For waste disposal the proper identify and choice of a suitable site is very crucial. Geological hydro-geological, topographical and climatologically factors will have to be taken into consideration. Large volume of hydrocarbons has to be cooled in oil refineries, at older refineries this is frequently done by a "once through" cooling water system. In such system water is taken from surface water sources used in heat exchange equipment and then discharged into the original water source through a separate outlet .The volume needed may be as high as 30 times the volume of crude processed depending on refinery complexity. A small part of the water which is used for cooling of pump seals may contain some oil. Modern refineries have either air cooling or recirculation cooling water system. The water used for direct cooling of hydrocarbon streams through heat exchangers is re-circulated after having been cooled in cooling towers, some water is lost by evaporation, and the required water for make-up is lost by amount to about 5% of the total volume per cycle. As a result salts and suspended solids gradually accumulate in the system. Blow down water is a slip at ream removed from the system to prevent accumulation of suspended and dissolved solid. For modern refineries amount is less than 0.1 tone of water per ton of crude processed. This water has been in close contact with processing streams and originates from steam stripping, crude oil washing and some chemical oil treatment processes. It contains variable amounts of oil and soluble material such as ammonium sulphide, phenols, organic acids and inorganic salts such as sodium chloride. Water requirements can be further reduced by incorporation of air cooling, the design stage should also involve an assessment facilities with a view to segregation is generally a features in modern refineries where some older refineries lake segregation and cannot achieve a comparable standard of aqueous effluent quality.

Process water is generally the major contaminated stream requiring treatment. Cooling water may become contaminated accidentally as a result of leakage. Therefore sound design of equipment, careful inspection and appropriate operating and maintenance procedures are essential to the control of hydrocarbon discharges in water. This is particularly true for recycled water. The waste-water treatment facilities in most refineries consisted of graving separators for the recovery free oil and sometimes strippers for the reduction of odor of sour condensates. Possible sequence for treatment of aqueous effluents from refineries (figure 3) the two main end products are sludge and water. If all of the steps illustrated were applied and were functioning properly for typical waste-water from an oil refinery, the resulting effluent would be of very high quality indeed, containing possibly less than 5 mg oil per liter. Table (1.2) indicates some approximate levels of contaminants that might be expected with different water treatment facilities. Water consumption in a new refinery can be reduced by cooling with air and recirculation water. The effluent or the spent chemicals from one unit can be recycled in the same unit or re-used in another unit. For example, spent caustic can be use for crude desalting, equipment and operating procedures may also be modified to reduce the concentration of impurities in the water like heavily contaminated stream from a bitumen unit could be heavily contaminated and small in volume.

Khartoum Refinery Company (KRC) Limited is a joint venture between China National petroleum Corporation (CNPC) and the Ministry of Energy & Mining (MEM) of Sudan, each holding fifty percent in shares. The joint venture agreement for the refinery was officially started on May 1998. The plant was formally put into production on May 2000.and the annual output is 2.2587 metric tons /year oil product such as gasoline, jet fuel, diesel, fuel oil and liquefied gas. The gasoline is unleaded; diesel is of high quality with low sulfur, low aromatics and light color. Due to low sulfur content, LPG is a clean fuel satisfying the environment protection requirements.

The unit processes the atmospheric residue of Sudan mix crude oil with capacity of 180 million metric tons /year. The unit consists of the fluid catalytic cracking, dry gas and liquefied petroleum gas (LPG), LPG and gasoline. RFCC has a 70% capacity of the total refinery. The capacity of the unit is 0.15 million metric tons /year (per 65-165^{o}C cut in the feedstock). The feed stock of the unit is the straight run naphtha oil from the Sudan mix crude oil.

The main product is gasoline with high Research Octane Number (RON) ninety one, by-product is gases consisting of hydrogen, LPG gas. The capacity of the unit is 0.5million metric ton /year; Feedstock of hydro fining is RFCC diesel.

Oily water comes from the process oily water of each production unit, drain oily water of each unit, dewatering process of the oil tank farm, oily rain, over flow water from column bottom pool, and back wash water from the filter pool of the circulation water plant. Caustic wastewater stores in the surge drum first and then enters into the neutralization pool slowly according to pH value, add acid to neutralize and then to the oily waste water system. The total purified compression air capacity is 197.7Nm^3/min unpurified compression air capacity is 107.1N m^3 / min. Cooling Compressed air, removing water and carbon dioxide (CO_2) in air, air cooling to liquefied temperature, air liquefying fractions, removing hazard pollutant in air.

For treatment sour water from all processing units enters sour water system and sent into sour water stripping unit. Oily water and alkaline water gather in oily water system and alkaline water system and then enter into wastewater treatment unit. Wastewater from living area and control rooms treated in cesspool then sent by domestic wastewater system into wastewater treatment plant. Production wastewater system collects wastewater from cooling towers; domestic wastewater not polluted by oil, sulfur and phenols, this kind of wastewater is drained into wastewater treatment plant and then pumped into lagoon out of the refinery without treatment.Sour water from all processing units treated in sour water stripping unit with a capacity 400,000 tone/year then 49.6t/h could be reused and the other would be sent into wastewater treatment plant. After pre-treatment wastewater containing pollutant would drain into wastewater treatment for final treating. Then drain into lagoon to meet the national emission control regulation. (COD: 100 mg/L ; Oil content 10mg/L; BOD : 20 mg/L ; NH_3 : 15 mg/L sulfide :1 mg/L ; Volatile phenols : 0.5 mg/L ; pH value(6-9) as shown in table(1.6).

Wastewater treatment plant is the main environment protection facility to degrade pollutants in water. The capacity is 300t/h. The oily water from processing unit into wastewater treatment plant will be pumped by oily water pump into oil separator, first stage and second stage floating pools to remove surface oil and some other pollutants. Then enter biological pool to remove phenols containing in wastewater. It is now allowed to enter into discharge pool. Lagoon: Khartoum Refinery Company limited built three lagoons to treat wastewater from treatment plant and production wastewater. Wastewater in lagoon would not be discharged and Leak but vaporized. The total capacity is 300tone/hour with a dimension three ponds for each (650 × 420 × 2.2) m^3. Active sludge, scum and sludge from waste water treatment plant dewatered in concentrator and sent into dehydrator by screw pump. By dehydration water content been 84-88% and volume reduced 20 times. Slop oil from sampling of all processing units and storing tanks sent into slop tanks. Other invaluable solid buried in specified plant about 12 Kilometer far away from the refinery to the east side.

MATERIALS AND METHODS

Twenty samples were collected from different four locations include:

i. Grid pond which was the first step for collection of waste water before treatment. Main facilities were to collect big suspended material.
ii. Physical treatment unit
iii. Chemical treatment unit
iv. Oxidation pond out the refinery last one to the west.

Samples for phenol test collected in glass containers and for oil content in glass containers with adding of hydrochloric acid for preservation.

Laboratory analysis was done in Central Petroleum Laboratory (CPL) to measure the pollution parameter in waste water and comparing with specific standard limits.

The waste water samples were examined in accordance with the “Standard Methods for Examination of Water and Waste Water” 20 Edition and the following analysis was carried out:

1 -The pH was done in central petroleum laboratory using a fixed pH meter type CG841 SCHOTT

2 -For the oil content partition-gravimetric method (APHA) 5520 B was carried out as for the sample preservation was done by adding 1:1 concentrated sulphuric acid to pH <2. (N-Hexane) used for extraction of waste water sample for oil content.
3 -The instrument used for measuring the phenols content is DR/4000 UV- spectrophotometers which calculate the concentration according to sample absorbance refer to Beers law:
4 -Total Suspended Solids Dried at103-105 ^{0}C APHA method 2540 D
5 The sulphide was measured using the methylene blue method under HACH program 3500 for sulphide (S^{2-}) (at wavelength (λ) 665nm).
6 -Chemical Oxygen Demand (COD).The chemical oxygen demand was rapidly measured calorimetrically using DR/4000 spectrophotometer (HACH) method (Rand, et.al, 1976).
7 Biological Oxygen Demand. (BOD).Biological oxygen demand is a measure of relevant oxygen requirements of waste water effluent and polluted water for biochemical degradation of organic material. The test takes five days incubation at 20 ^{0}C.
8 -Nessler method (HACH) 8030 was used to measure nitrogen and ammonia at wavelength (λ) 425nmusing DR/ 4000 spectrophotometer.
9 -Nitric acid digestion method (APHA 303E) was used to determined the trace elements contents by atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Khartoum refinery is a complex refinery, design typically to process Sudanese crude or Nile blended. Total capacity of the refinery is 50000 barrel per day. There is a new extension with capacity of 20000 barrel per day. The main product of the refinery is motor gasoline unleaded with high octane number (91.5), liquefied petroleum gas (LPG), gas oil and turbine jet fuel. The refinery operates continuously for 24 hours.

The refinery is located 15 kilometer north east of Al-gaily city in a semi rocky desert land about 12 kilometers from Nile River. There are two valleys on both sides of the refinery flow direct to the river.

The waste treatment unit for water is design in modified way by collection of waste water and separation for alkali and acidic water to be neutralize, then skimming of oil from the water. This waste water passes into biochemical unit for further treatment to get rid of the polluted materials.

Table (1) Analysis of the effluent stream from grid pond before treatment in Khartoum refinery
Flow rate = 300 m^3 / hour

ITEM	pH	OIL mg/l	COD mg/l	TSS mg/l	SULPHIDE mg/l	NH_3-N mg/l	PHENOL mg/l
Sample (1)	8.9	500.3	341	84	0.0	13.3	39.4
Sample (2)	7.8	606.2	577	52	0.1	10.1	23.5
Sample (3)	8.1	1123.8	443	40	3.2	15.4	14.3
Sample (4)	8.4	1322.8	317	32	1.2	12.8	12.9
Sample (5)	8.9	400.2	440	93	1.3	14.4	13.5
Average	8.4	790.7	424	60	1.2	13.2	20.7

a) The grid pond was the first step in the physical treatment.
b) It had ability just to remove the heavy suspended materials.
c) Oil content790.7 mg/l, phenol, COD, and nitrogen ammonia had high concentration.

Table (.2) Analysis of the effluent stream from physical treatment unit in Khartoum refinery

ITEM	pH	OIL mg/l	COD mg/l	TSS mg/l	SULPHIDE mg/l	NH3-N mg/l	PHENOL mg/l
Sample (1)	7.1	53.8	272.0	41.0	0.50	3.2	0.1
Sample (2)	6.2	285.7	381.0	32.0	0.80	10.1	0.2
Sample (3)	7.6	121.1	117.0	29.0	1.10	15.4	0.3
Sample (4)	6.2	183.7	91.2	18.0	0.50	12.8	0.5
Sample (5)	7.6	179.0	57.0	93.0	0.01	13.3	0.2
Average	6.9	164.7	183.6	42.6	0.58	11.0	0.3

a) This unit contains one house called (house 1) in which the pH of the waste water examined and classify to acidic and alkali water in two separated tank.
b) Acidic water treated by alkali water and alkali water neutralized by sulphuric acid (H_2SO_4). Now this stopped because high cost of H_2SO_4
c) This unit had oil separated tank which separated the oil from water by skimmer. The oil content decrease to value 164.7 mg/l.

Table (3) Analysis of the effluent stream from biochemical treatment unit in Khartoum refinery

ITEM	pH	OIL mg/l	COD mg/l	TSS mg/l	SULPHIDE mg/l	NH3-N mg/l	PHENOL mg/l	BOD5 mg/l
Sample (1)	5.7	13.9	124	70	0.1	9.6	0.10	15
Sample (2)	7.8	15.1	133	57	0.2	7.2	0.20	14
Sample (3)	6.2	10.9	75	62	0.3	8.2	0.10	23
Sample (4)	7.9	17.1	177	100	0.1	3.2	0.01	15
Sample (5)	7.6	9.4	57	93	0.1	6.2	0.05	23
Average	7.0	13.3	113	76	0.1	6.9	0.09	18

a) The treatment in this unit was done by bacteria in two ways aerobic and anaerobic.
b) In this unit the oil content decreased to13.3 mg/l from 164.7 mg/l.
c) phenol content average also 0.09mg/l

Table (4) Analysis of the waste water combined sample from the three oxidation ponds outside Khartoum refinery

ITEM	Ph	OIL mg/l	COD mg/l	TSS mg/l	SULPHIDE mg/l	NH3-N mg/l	PHENOL mg/l	BOD5 mg/l
Sample (1)	8.7	25	351	100.0	0.02	5.4	0.04	23
Sample (2)	9.2	5	193	42.0	0.01	0.6	0.08	8
Sample (3)	7.7	13	193	93.0	0.01	0.6	0.01	12
Sample (4)	9.5	8	162	230.0	0.03	0.8	0.01	15
Sample (5)	9.6	4	173	44.0	0.02	6.7	0.02	26
Average	8.9	11	214	101.8	0.02	2.8	0.03	17

a) The oil content 11mg/l which exceed the standard value in appendix (1) which value should be 10 mg/l
b) The value of COD 214 mg/l also in the standard should be 150 mg/l.
c) TSS value 101.8mg/l , standard limits is 30 mg/l

Table (5) Analysis of the waste water combined sample from the three oxidation ponds outside Khartoum refinery

Heavy metals by atomic absorption spectroscopy (AAS) in part per million (ppm)

ITEM	SAMPLE (1) ppm	SAMPLE (2) ppm	SAMPLE (3) ppm	SAMPLE (4) ppm	SAMPLE (5) ppm
Pb	0.10	< 0.10	0.10	0.10	< 0.10
Cd	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
As	< 0.03	< 0.03	< 0.03	<0.03	< 0.03
Cr	< 0.06	< 0.07	< 0.06	0.10	< 0.06
Cu	0.00	0.04	0.03	0.02	0.03
Ni	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
V	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Fe	0.70	0.77	1.00	0.70	0.70
Se	< 5.00	< 5.00	< 5.00	< 5.00	< 5.00
Zn	0.10	0.08	0.10	0.10	0.10
Ag	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02

a) The concentration of trace element complies with the limits of the standard in appendix(1) and (2) except: Iron, lead and chromium concentration exceeded maximum limits in appendix (1) and (2) it need to be more treated.

Table (6) comparison of the average quantities of mentioned parameter for the four units in wastewater treatment in Khartoum refinery

ITEM	pH	OIL mg/l	COD mg/l	TSS mg/l	SULPHIDE mg/l	NH3-N mg/l	PHENOL mg/l
GRID POND	8.42	790.66	423.6	60.2	1.17	13.20	20.72
PHYS. UNIT	6.94	164.66	183.6	42.6	0.58	10.96	0.26
BIO. UNIT	7.04	13.28	113.2	76.4	0.15	6.88	0.09
OXIDATION POND	8.94	10.94	214.4	101.8	0.02	2.82	0.03

Figure (3.1) pH value in waste water treatment units in Khartoum refinery

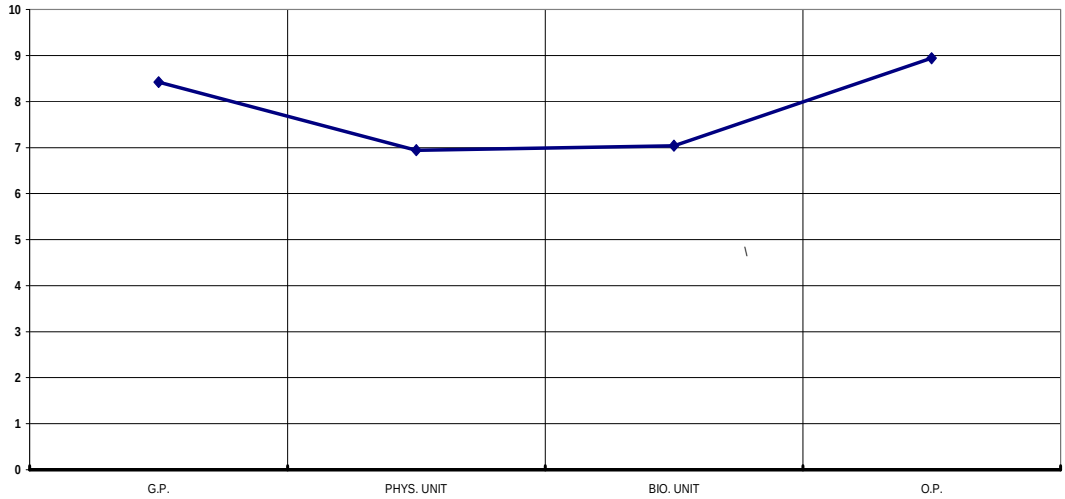
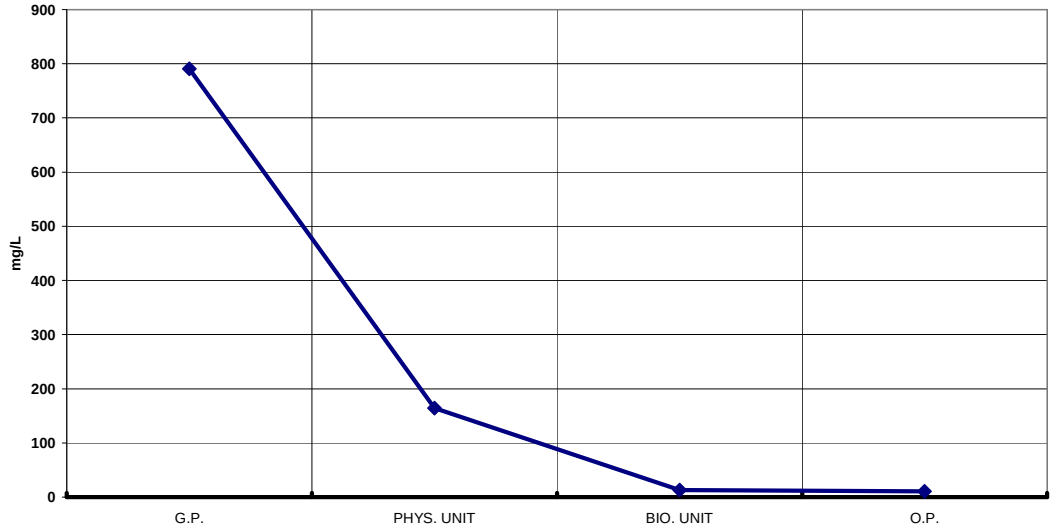


Figure (3.2) Oil content in waste water treatment units in Khartoum refinery in mg/l



a) From figure (3-1) the p H value decrease in physical treatment unit for neutralization of sour water then increase in oxidation pond to reach the maximum limit.
b) From figure (3-2) oil content also decreases but it exceeds the standard limit in oxidation pond so the physical treatment unit could be more efficient by using compact flotation unit (CFU).

c) From figure (3-3) chemical oxygen demand (COD) very high and this indicates that high quantity of chemicals in the waste.
d) From figure (3-4) total suspended solids (TSS) 101.8 mg/l also exceed the standard limit 30 mg/l.
e) Phenol, nitrogen ammonia and sulphide within the limits in the final disposals.

Figure (3.3) Chemical oxygen demand (COD) in waste water treatment units in Khartoum refinery in mg/l

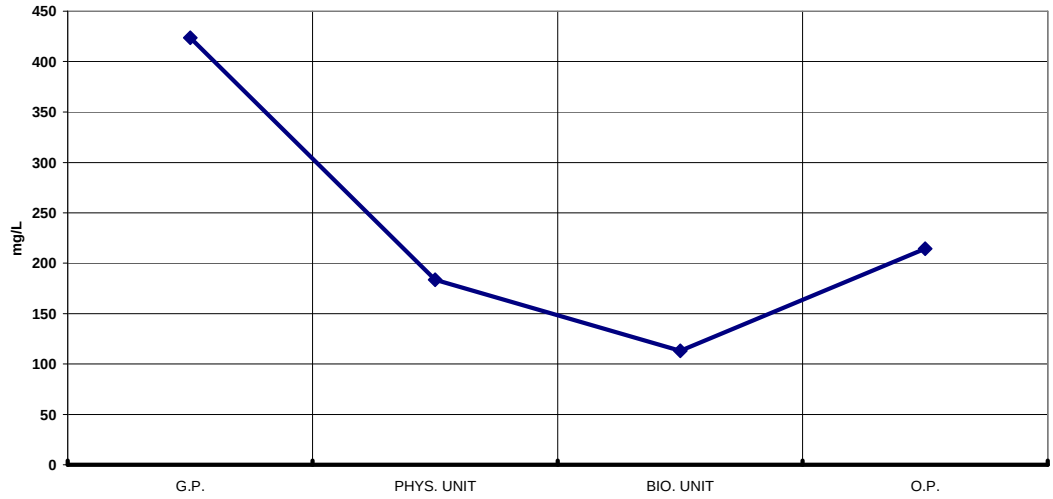


Figure (3.4)Total susbended solid (TSS) content in waste water treatment units in Khartoum refinery in mg/l

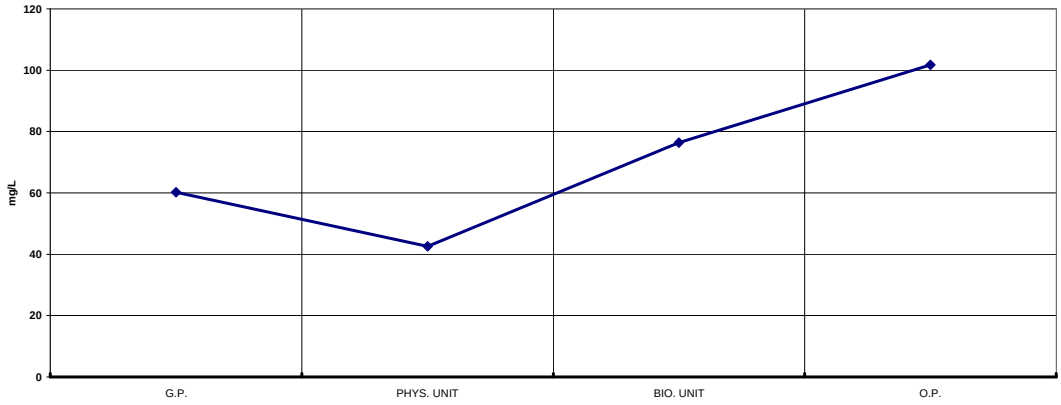


Figure (3.5)Sulfphide content in waste water treatment units in Khartoum refinery
in mg/l

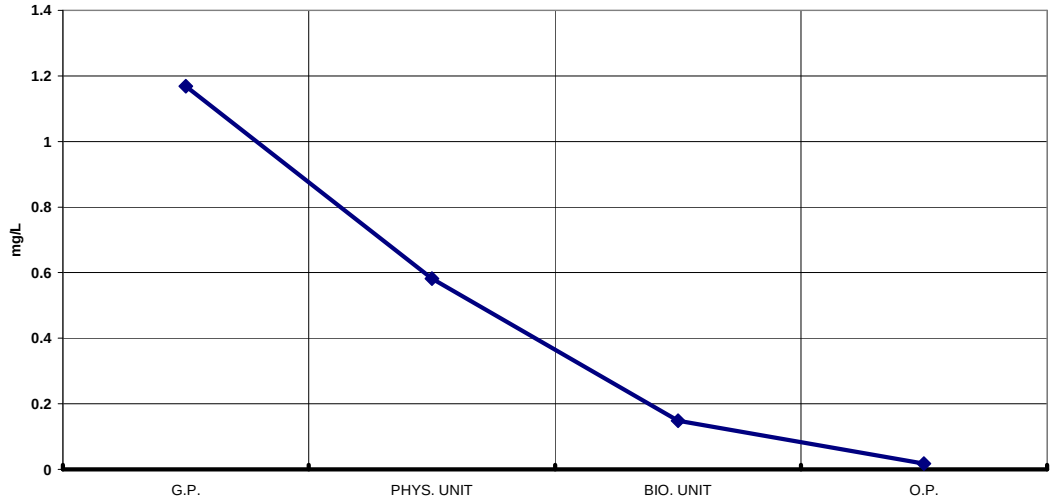


Figure (3.6) Nitrogen- ammonia (NH3-N) content in waste water treatment units in Khartoum refinery in mg/l

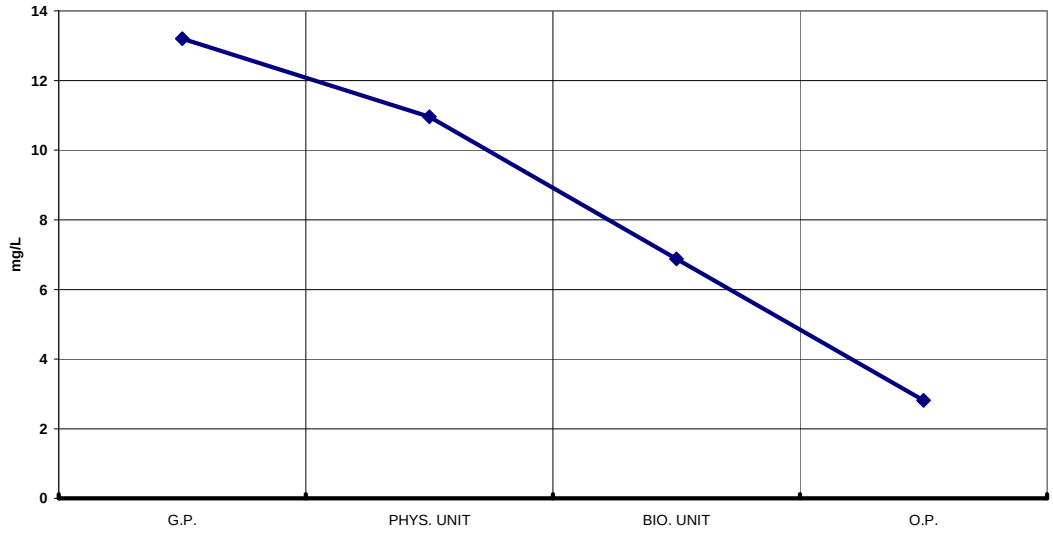
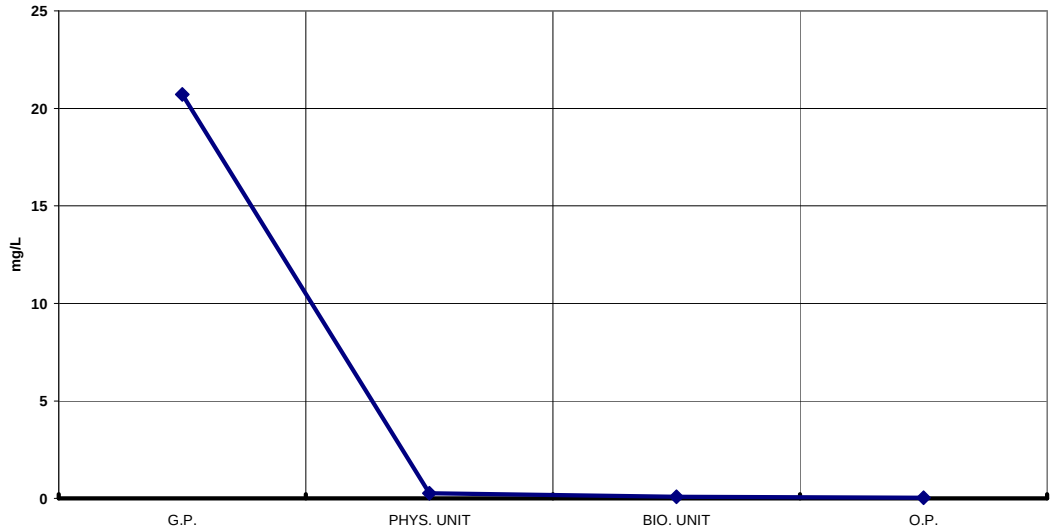


Figure (3.7) Phenol content in waste water treatment units in Khartoum refinery in mg/l



CONCLUSION

1. From the study the fallowing conclusion obtained:

a) The waste generated from Khartoum Refinery is in a big quantity because it is a complex refinery

b) The Sudanese crude has very low sulphur content 0.0635 % and about 0.07% in atmospheric residue so that SO_X emissions are expected to be in low levels but with the development of the refinery expected the SO_2 from the flare to be 315 kg/h so sulphur recovery unit necessary to be build.

c) H_2S is only monitoring by personnel detectors.

d) No monitoring for other gases e.g., NO_X, SO_X, CO.

e) Ammonia recovered in sour water stripping unit and flows out in ammonia solution (NH_3 content 18%).Some is used in CDU unit and the remaining quantity is drained out side the refinery.

f) The flare is set up to meet the need of all units with heights of 100m.

g) Biological treatment is applied to the waste water.

h) The domestic sanitary water also joins the refinery waste water discharge.

i) The capacity of the three oxidation pond is = 2,020,200 m^3.

a. The quantity of coming water from the refinery /day =11040

b. The quantity of the evaporated water /day = 6800

c. The remaining quantity in the oxidation pond /day = 4240

d. Number of days need to fill oxidation ponds = 476

j) The average concentration of suspended solid (ss) is 101.8 mg/l and chemical oxygen demand (COD) is 214.4 in the oxidation pond both of them are high.

k) Oil and Grease average is 10.94 mg/l which also exceed the maximum limit.

l) Heavy metals e.g. iron ,chromium and lead has a maximum values.

m) Khartoum refinery is located between two valleys.

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